SYNTHESIS AND STEREOCHEMICAL STUDIES OF SOME METAL COMPLEXES WITH HETEROCYCLIC N—CONTAINING LIGANDS

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Certified that the work embodied in this dissertation entitled " Synthesis and Stereochemical Studies of some Metal Complexes with Heterocyclic N-containing Ligands" is the result of the original research work carried out by Mr. Mohd Akhtar Zahoor under my supervision and is suitable for submission for the M.Phil. degree of Aligarh Muslim University, Aligarh.

(S.A.A. Zaidi)

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PUBLICATION

1. Synthesis and characterization of potassium dihydrobis-, potassium hydrotris- and potassium tetrakis(indolyl) borates and their complexes with some transition metal ions.

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INTRODUCTION

Well documented boron-nitrogen chemistry postulates are supplemented by experimental evidences. Although they were discovered way back in the nineteenth century (1), yet the chemistry of the compounds containing boron-nitrogen bond has experienced an impressive renaissance only over the last two decades. Most of the efforts have been centered round the nature of the boron-nitrogen bond and the resulting properties of the compounds containing such bonds. A spate of research activity in this area during the past decade resulted in an exponential growth of publications of research articles, reviews (2-7) and books (8,9) on the different aspect of boron-nitrogen chemistry.

The area of poly organoborate chemistry emerged only about two decade ago by the pioneering work of Trofimenko who established a series of novel poly(1-Pyrazolyl) borates (10), a new class of chelating ligands leading to the development of a new sub area. A number of transition metal complexes incorporating pyrazolyl borate ligands have since been reported (11-14).

The synthesis and physico-chemical studies of salts, acids and coordination complexes derived from uninegative ligand of general formulae $[H_nB(P_z)_{4-n}]^-$ where n = 0, 1 or 2 and 'P_z' stands for pyrazolyl residue, have been reported (15). It has been shown that when n=2, the ligand is bidentate, while n=3 gives the tridentate ligand with C_{3v} symmetry.

The dihydrobis (1-Pyrazolyl) borate anion forms chelates with divalent first row transition metal ions (16). The isomorphous Ni(II) and Cu(II) chelates have been assigned square planar geometry whereas the chelates of Mn(II), Co(II) and Zn(II) were octahedral (16).

The hydrotris(1-Pyrazolyl) borate anion, $HBPz_3^-$ is unique in being the only known trigonally tridentate uninegative ligand (11,17). Its complexes with Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) ions were assigned octahedral geometry. A cross over between high spin and low spin states has been observed in $Fe[HBPz_3]_2$ (18).

The tetrakis (1-Pyrazolyl) borate anion, BPz_4^- in terms of coordination ability, has shown to be merely a substituted variant of hydrotris (1-Pyrazolyl) borate. These complexes are however, thermally more stable and have somewhat lower solubility than those of the corresponding hydrotris complexes. The BPz_4^- can also act as a tetradentate donor group when a pair of N-termini are bridged by appropriate four coordinate species. Like the hydrotris ligand it yields half sandwich compounds (18,19).

The anionic pyrazolyl derivatives of aluminium and gallium as chelating ligands and a wide range of their complexes have been isolated and characterized (20-24). The nickel complex of gallate ligand is reported to be a non rigid square planar molecule. Minghetti and coworkers (25) have synthesized platinum (II) Pyrazolide complex. The heteropolymetallic systems involving

transition metals have given rise to a series of very interest- and novel compounds(26-29). The kinetics and mechanism of the hydrolysis of Phenyl (Pyrrolyl-1) borate, hydro (Pyrrolyl-1) borate and cyano (Pyrrolyl-1) borate has also been reported recently (30-31).

The investigations on Poly (1-Pyrazolyl) borates have been further extended towards the synthesis of dihydrobis, hydro- tris- and tetrakis ligands by using indazoles and thiazoles by Zaidi and coworkers (32-36). Octahedral complexes of the type $M[HBInz_3]_2$ with several transition metals have been synthesized. The Cu(II) Complex has been assigned a square planar geometry. The tetrakis(indazolyl) borate complexes of Cu(II), Ni(II), Co(II), Mn(II) and Fe(III) ions resemble their hydrotris analogue (37). A series of analogous ligands using 5-, 6-, nitro-indazoles and 2-mercaptobenzothiazole have been synthesized and their coordinating properties discussed (35,36). The nitro group of the indazole in nitroindazolyl borate remains uncoordinated.

Recent work in these laboratories has led to the synthesis of poly(imidazolyl) borate anion and a number of their complexes with various metal ions (38-40). The dihydrobis (imidazolyl) borate complexes with Mn(II), Co(II), Ni(II), Cr(III) and Fe(III) give rise to octahedral geometry while those of Zn(II), Cd(II) and Hg(II) are apparently tetrahedral and Cu(II) has a square planar geometry.

The hydrotris (imidazolyl) borate anion $[HBIz_3]$ yielded a number of complexes with Cr(III), Mn(II), Fe(III), Co(II) and

Ni(II). Probably these chelates have octahedral structure while that of Cu(II) is square planar.

The complexes of tetrakis (imidazolyl) borate anion, $[BIz_4]$ with Mn(II), Fe(III), Co(II) and Ni(II) are octahedral while that of Cu(II) have square planar geometry.

The chemistry of indole had its beginning in the preparation of dyes and thus for a number of years was intimately associated with it. Today the scope of Indole Chemistry is indeed multifarious extending from rather simple parent indoles, through condensed system such as Carbazole, Oxygenated indole derivatives, to highly complex naturally occurring materials.

Indole derivatives and their metal chelates have attracted special attention due to their activities against tumour growth, skin diseases (41,42) and as anti inflammatory agent in bone fracture repair in rats (43) and in many metabolic disorders in Urine (44).

Recently some important developments have taken place in the toxicological aspects of indole and its derivatives. Particularly work has been done on the chemical nature and sites of toxic actions of these compounds, the effect of molecular structure on their biological activity and finally their biochemical and environmental effect.

The biological activity pattern of the five unsubstituted indole-1-glucosides 4,3-substituted 1-β-D-glycopyranosyl indole and substituted indole 1-α-L arabinosides and 6-nitroindole

glycosides were compared for cytotoxic effects on monolayer cultures of human Ovarian Carcinoma Cell line. The indole 1-α-L arabionosides has the greatest cytotoxic effect, the most active compounds being 1-α-L arabinopyranosyl-6-nitro-indole (45).

The urinary level of indole melanogen were higher in patients with several skin diseases, psoriasis, porphyrias, basal cell, carcinoma and subjects of black race than those of normal subjects of white race or patients with spinalioma (46).

Indole and its analogues have chlorophyll dependent oxidation in triton x-100 solubilized chloroplasts showed high rates of light dependent oxygen uptake when indoleacetic acid was present. The chlorophyll dependent oxidation of various indoles and other non indolic analogues of indole acetic acid has also been tested. Indole acetic acid and other carboxylated indoles showed high rates of oxidation whereas oxidation of indoles without a free carboxyl group was slow (47).

The Complexes of Indoles with several transition metals have been reported to have significant biological properties. The copper complex exhibits a corrosion inhibiting properties. A 0.1 N HOAC and chloro, dichloro and trichloro acetic acid, 2-methyl benzothiazole and indole mixtures can be used as corrosion inhibitor of copper. The stability constants of the complexes were potentiometrically determined to show that

the inhibition efficiency increases with an increase in the stability constant and also the basic strength of the ligand (48).

The role of indole in 2-acetylaminofluorene bladder tumorigenesis was crit. evaluated in hamsters. To avoid the influence of a nutritional factor on tumor incidence, the animals were pair-fed for 8,10 and 12 months. Addition of indole to the diet resulted in a higher incidence of bladder tumors in both males and females. Indole definitely increased the bladder tumor incidence at 8 months. The tumor incidence was higher in males than in females irrespective of the diet administered. Indole did not alter the urinary output of N-hydroxy 2-acetylaminofluorene in males (41).

PRESENT WORK

The work carried out in our laboratories had led to the synthesis of a number of B-N bonded ligands of the type $[H_nB(I_z)_{4-n}]^-$ where I_z = indazole or imidazole and n=0, 1 or 2. A large number of their complexes with a variety of metal ions have been characterized.

In extending our work on the chemistry of B-N bonded heterocycles it was considered worth while to synthesize Potassium dihydrobis-, Potassium hydrotris and Potassium tetrakis (indolyl) borates with a view to examining their coordinating ability with Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) metal ions.

EXPERIMENTAL

MATERIAL AND METHODS

Indole (Wilson) was used without further purification. Metal salts (BDH, Analar) were used as received. Dimethyl formamide (E.Merck) was dried over potassium hydroxide and then vacuum distilled.

Preparation of Potassium Dihydrobis(Indolyl)Borate

Potassium borohydride (0.46g, 8.50 mmol) and indole(2.00g, 17.0 mmol) in 1:2 molar ratio were refluxed in dry DMF(~30 ml) for about twelve hours till 17.0 mmol of hydrogen gas was evolved. The reaction may be represented as below.

$$2C_8H_7N + KBH_4 \longrightarrow K^+(C_{16}H_{14}N_2B)^- + 2H_2$$

After the reactions was complete, the solution became dark violet. The reaction mixture, on cooling to room temperature yielded a colourless solid which was filtered washed and dried in vacuo. Yield 74%, Decomposition temperature 285°C.

Preparation of the Complexes

The ligand solution was prepared by adding ~25 ml water to the cooled suspension of ligand in DMF in each case.

[Chloro-bis(dihydrobis indolyl)borato] chromium(III), $[Cr(C_{16}H_{14}N_2B)_2Cl]$

The ligand solution (3.78 mmol) and aqueous chromium(III) chloride (1.89 mmol) were mixed together and refluxed for about

eight hours. A brown product obtained was filtered, washed and dried in vacuo. It decomposes without melting at 284°C, Yield 72%.

[Chloro-dihydrobis(indolyl) borato] manganese(II), $[Mn(C_{16}H_{14}N_2B)Cl]$

A mixture of the ligand (3.78 mmol) and manganese(II) chloride solution (3.78 mmol) was refluxed for about eight hours. A brown product precipitated which was filtered off, washed and finally vacuum dried. Decomposition temperature 278°C, Yield 68%.

[Chloro-bis(dihydrobis indolyl) borato] iron(III), $[Fe(C_{16}H_{14}N_2B)_2Cl]$

To potassium dihydrobis (indolyl) borate(3.78 mmol) was added an aqueous iron(III) chloride solution (1.89 mmol) the resulting suspension was refluxed for about eight hours. A yellow solid was filtered and dried in vacuo. It decomposes without melting at 280°C, yield 66%.

[Chloro-dihydrobis (indolyl) borato] cobalt(II), $[Co(C_{16}H_{14}N_2B)Cl]$

Cobalt(II) chloride solution (3.78 mmol) was added to the ligand solution (3.78 mmol) and the resulting solution was refluxed for about seven hours. A pink solid obtained, which was filtered, washed and dried in vacuum at room temperature. Decomposition temperature is 275°C, Yield 68%.

[Chloro-dihydrobis (Indolyl) borato] nickel (II), [$Ni(C_{16}H_{14}N_2B)Cl$]

The compound [$Ni(C_{16}H_{14}N_2B)Cl$] was prepared by adding the ligand solution (3.78 mmol) to nickel(II) chloride (3.78 mmol) and refluxed for about seven hours. A green product obtained, which was filtered, washed with ether and vacuum dried. It decomposes without melting at 276°C, Yield 69%.

[Chloro-dihydrobis (indolyl) borato] copper (II), [$Cu(C_{16}H_{14}N_2B)Cl$]

A hot solution of Potassium dihydrobis(indolyl) borate (3.78 mmol) was mixed with copper(II) chloride solution(3.78 mmol) and refluxed for about eight hours. It yielded a green solid. It decomposes without melting at 270°C, yield 71%.

[Chloro-dihydrobis(indolyl) borato] zinc (II), [$Zn(C_{16}H_{14}N_2B)Cl$]

The preparation of this complex was achieved by refluxing zinc(II) chloride (3.78 mmol) and ligand solution (3.78 mmol) in DMF for about seven hours. The resulting colourless product was obtained, filtered and dried in vacuo. It decomposes without melting at 281°C, Yield 67%.

The complexation may be represented as below:

$$2K^+(C_{16}H_{14}N_2B)^- + MCl_3 \longrightarrow [M(C_{16}H_{14}N_2B)_2Cl] + 2KCl$$

where M=Cr(III), Fe(III)

$$K^{+}(C_{16}H_{14}N_2B)^{-} + MCl_2 \longrightarrow [M(C_{16}H_{14}N_2B)Cl] + KCl$$

where M=Mn(II), Co(II), Ni(II), Cu(II), Zn(II).

Preparation of Potassium Hydrotris (Indolyl) Borate.

Potassium borohydride (0.30g, 5.70 mmol) and indole (2.00g, 17.10 mmol) in 1:3 molar ratio were refluxed in dry DMF(~50 ml) for twenty four hours till 17.10 mmol hydrogen gas was evolved according to the equation.

$$3C_8H_7N + KBH_4 \longrightarrow K^{+}(C_{24}H_{19}N_3B)^{-} + 3H_2$$

On cooling the contents a white solid material separated out. This was filtered, washed and dried under reduced pressure at room temperature. yield 68%, Decomposition temperature 296°C.

Preparation of the Complexes.

The ligand solution was prepared by adding~30ml water to the cooled suspension of ligand in DMF in each case.

[Chloro-bis(hydrotris indolyl) borato] chromium(III), $[Cr(C_{24}H_{19}N_3B)_2Cl]$

To a solution of hydrotris(indolyl) borate(2.62 mmol) was added chromium(III) chloride solution (1.31 mmol) in DMF and the mixture was refluxed for about seven hours. A brown solid thus obtained, was filtered off and dried in vacuo, Yield 68%, Decomposition temperature 275°C.

[Chloro-hydrotris(indolyl) borato] manganese(II), $[Mn(C_{24}H_{19}N_3B)Cl]$

Preparation of the above compound was accomplished by refluxing the manganese(II) chloride (2.62 mmol) and the ligand solution (2.62 mmol) in DMF for about eight hours. A brown solid was obtained by filtration. It was vacuum dried. Yield 68%, Decomposition temperature 280°C.

[Chloro-bis(hydrotris indolyl) borato] iron(III), $[Fe(C_{24}H_{19}N_3B)_2Cl]$

The complex $Fe(C_{24}H_{19}N_3B)_2Cl$ was prepared by refluxing the stoichiometric amount of iron(III) chloride (1.31 mmol) and the ligand solution (2.62 mmol) for about seven hours. The solid thus obtained was filtered, washed and dried in vacuo. Yield 64%, Decomposition temperature 278°C.

[Chloro-hydrotris (indolyl) borato] cobalt(II), $[Co(C_{24}H_{19}N_3B)Cl]$

Cobalt(II) chloride solution (2.62 mmol) was added to the ligand solution (2.62 mmol) which after refluxing for about seven hours gave a pink solid. The compound was isolated in the manner described above. Yield 76%, Decomposition temperature 283°C.

[Chloro-hydrotris(indolyl) borato] nickel(II), $[Ni(C_{24}H_{19}N_3B)Cl]$

An aqueous solution of nickel(II) chloride (2.62 mmol) was added to the ligand solution (2.62 mmol) and refluxed for about

six hours. A green solid appeared which was isolated by filtration and finally vacuum dried. Yield 68%, Decomposition temperature 270°C.

[Chloro-hydrotris(indolyl)borato] copper(II), $[Cu(C_{24}H_{19}N_3B)Cl]$

The ligand solution (2.62 mmol) and copper(II) chloride solution (2.62 mmol) in DMF were mixed together and refluxed for about six hours. The reaction mixture was allowed to cool to room temperature. A green complex appeared which was then filtered off, washed and finally vacuum dried. Yield 74%, Decomposition temperature 285°C.

[Chloro-hydrotris(indolyl) borato] zinc(II), $[Zn(C_{24}H_{19}N_3B)Cl]$

A solution of zinc(II) chloride (2.62 mmol) was added to the ligand solution (2.62 mmol) and the contents refluxed for about seven hours. A white solid appeared which was isolated by filteration and then washed repeatedly with DMF and then dried in vacuo, Yield 74%, Decomposition temperature 285°C.

The complexation may be represented as below:

$$2K^+(C_{24}H_{19}N_3B)^- + MCl_3 \longrightarrow [M(C_{24}H_{19}N_3B)_2Cl] + 2KCl$$

where M=Cr(III), Fe(III)

$$K^+(C_{24}H_{19}N_3B)^- + MCl_2 \longrightarrow [M(C_{24}H_{19}N_3B)Cl + KCl$$

where M=Mn(II), Co(II), Ni(II), Cu(II), Zn(II)

Preparation of Potassium Tetrakis(Indolyl) Borate

Potassium borohydride (0.23g, 4.25 mmol) and indole (2.00g, 17.00 mmol) were refluxed in dry DMF(~60 ml) for about forty eight hours when 17.00 mmol of hydrogen gas was evolved. The reaction may br represented as

$$4C_8H_7N + KBH_4 \longrightarrow K^+(C_{32}H_{24}N_4B)^- + 4H_2$$

The colourless solid material obtained on cooling the reaction mixture was filtered, washed and dried in vacuo. Yield 64% Decomposition temperature 280°C.

Preparation of the Complexes

The solution of the ligand was prepared in aqueous DMF (50:50, V/V).

[Chloro-bis(tetrakis indolyl) borato] chromium(III), $[Cr(C_{32}H_{24}N_4B)_2Cl]$

A mixture of the ligand solution (2.12 mmol) and an aqueous solution of chromium(III) chloride (1.06 mmol) was refluxed for about five hours. The precipitate so obtained on cooling to room temperature was filtered, washed and dried in vacuo yield 68%, Decomposition temperature 281°C.

[Chloro-tetrakis(indolyl) borato] manganese(II), $[Mn(C_{32}H_{24}N_4B)Cl]$

A solution of manganese(II) chloride(2.12 mmol) was added to a solution of the ligand (2.12 mmol) and the reaction run at reflux for about five hours. The precipitate appeared instant-

aneously which was filtered, washed and then vacuum dried. Yield 65%, Decomposition temperature 281°C.

[Chloro-bis(tetrakis indolyl) borato] iron(III), $[Fe(C_{32}H_{24}N_4B)_2Cl]$

A mixture of aqueous iron(III) chloride (1.06 mmol) and ligand solution (2.12 mmol) in DMF were refluxed for about six hours. A yellow complex was obtained. It was filtered washed and dried in vacuo. Yield 69%, Decomposition temperature 270°C.

[Chloro-tetrakis(indolyl) borato] cobalt(II), $[Co(C_{32}H_{24}N_4B)Cl]$

An aqueous solution of cobalt(II) chloride (2.12 mmol) was added to the ligand solution (2.12 mmol). The mixture was refluxed for about five hours. On cooling the contents the precipitate separated out and was filtered by suction and dried under vacuum. Yield 68%, Decomposition temperature 285°C.

[Chloro-tetrakis(indolyl) borato] nickel(II), $[Ni(C_{32}H_{24}N_4B)Cl]$

An aqueous solution of nickel(II) chloride (2.12 mmol) was mixed with the ligand solution (2.12 mmol) and refluxed for about five hours. The resulting green precipitate was filtered, washed and finally vacuum dried. Yield 72%, Decomposition temperature 280°C.

[Chloro-tetrakis(indolyl)borato] copper(II), $[Cu(C_{32}H_{24}N_4B)Cl]$

Equimolar solution of copper(II) chloride (2.12 mmol) and the ligand solution (2.12 mmol) were mixed together and refluxed for about five hours. A green compound which appeared

was worked up as described earlier. Yield 67%, Decomposition temperature 268°C.

[Chloro-tetrakis(indolyl) borato] zinc(II), $[Zn(C_{32}H_{24}N_4B)Cl]$

The ligand solution (2.12 mmol) and zinc(II) chloride solution (2.12 mmol) were mixed together and refluxed for about five hours. The reaction mixture was allowed to cool to room temperature. A solid complex appeared which was the filtered off, washed and finally vacuum dried. Yield 68%, Decomposition temperature 266°C.

The complexation may be represented as below:

$$2K^+(C_{32}H_{24}N_4B)^- + MCl_3 \longrightarrow [M(C_{32}H_{24}N_4B)\,Cl] + 2KCl$$

where M=Cr(III), Fe(III)

$$K^+(C_{32}H_{24}N_4B)^- + MCl_2 \longrightarrow [M(C_{32}H_{24}N_4B)Cl] + 2KCl$$

where M=Mn(II), Co(II), Ni(II), Cu(II), Zn(II)

Analysis and physical Measurements

The complexes were analysed for metal contents by standard procedure (49). Carbon, hydrogen and nitrogen analyses were carried out with Thomas and coleman analyser, carlo Erba 1106. The infrared spectra (4000–200 cm^{-1}) in KBr and Nujol respectively were recorded with a perkin-Elmer grating spectrophotometer model 621. The diffuse reflectance spectra were recorded with a carl-zeiss VSU-2P Spectrophotometer using MgO as calibrant and magnetic susceptibility measurements were done by the vibration sample magnetometer(VSM) technique.

RESULTS AND DISCUSSION

Potassium dihydrobis-, potassium hydrotris and Potassium tetrakis(indolyl) borates have been synthesized by the action of KBH_4 over indole in 1:2, 1:3 and 1:4 ratios. The completion of the reaction was ascertained by the release of requisite volume of hydrogen gas. Elemental analysis, colour, decomposition temperature and percent yield are listed in Tables I-III. The probable structure of these ligands is shown in Fig.1. They have been further characterized by their infrared spectra (Tables IV-VI). It is inferred from the disappearance of NH band (3400-3000 cm^{-1}) and the appearance of a new band of medium intensity at 1390 cm^{-1}, that hydrogen from NH of indole has been removed and a B-N bond formed (50). A doublet at 2420 and 2380 cm^{-1} due to two B-H bonds has been observed in potassium dihydrobis (indolyl) borate (51). There appears only one B-H band at 2410 cm^{-1} in hydrotris ligand and obviously there is no such band in tetrakis ligand as a consequence of removal of all hydrogens from KBH_4.

A band in the region 1352-1345 cm^{-1} has been assigned to the C-N stretching frequency which does not show significant shifts. However, after complexation small shifts in C-N are observed irrespective of the nature of metal ions coordinated (52). Ring stretching frequency appears in 1610-1620 cm^{-1} range.

Some new bands of weaker intensity observed in the far infrared region(430-380 cm^{-1}) of the complexes have been tentatively assigned to the metal-nitrogen stretching frequency(53).

Table I. Colour, Decomposition Temperature, % Yield and Analytical Data of the Complexes of Potassium Dihydrobis(Indolyl)Borate.

Compounds	Colour	Decomposition Temp. (°C)	Yield (%)	Analysis(%) Found(Calcd.)				
				C	H	N	M	Cl
$K^+(C_{16}H_{14}N_2B)^-$	Colourless	285	74	67.12 (67.60)	4.81 (4.92)	9.96 (9.87)	-	-
$Cr(C_{16}H_{14}N_2B)_2Cl$	Brown	281	72	64.84 (66.49)	4.83 (4.85)	9.54 (9.69)	8.87 (9.00)	6.07 (6.05)
$Mn(C_{16}H_{14}N_2B)Cl$	Brown	278	68	57.32 (57.23)	4.12 (4.17)	8.19 (8.35)	16.29 (16.39)	10.47 (10.58)
$Fe(C_{16}H_{14}N_2B)_2Cl$	Yellow	280	66	65.95 (66.05)	4.73 (4.82)	9.67 (9.63)	9.53 (9.63)	6.12 (6.11)
$Co(C_{16}H_{14}N_2B)Cl$	Pink	275	68	55.43 (56.55)	4.03 (4.13)	8.17 (8.25)	17.34 (17.31)	10.33 (10.46)
$Ni(C_{16}H_{14}N_2B)Cl$	Green	276	69	55.38 (56.60)	4.14 (4.13)	8.15 (8.26)	17.19 (17.31)	10.35 (10.47)
$Cu(C_{16}H_{14}N_2B)Cl$	Green	270	71	56.18 (55.82)	4.98 (4.07)	8.05 (8.14)	18.38 (18.47)	10.19 (10.32)
$Zn(C_{16}H_{14}N_2B)Cl$	White	281	67	55.02 (55.51)	4.01 (4.05)	8.02 (8.09)	18.73 (18.90)	10.14 (10.26)

Table II. Colour, Decomposition Temperature, % Yield and Analytical Data of the Complexes of Potassium Hydrotris(Indolyl) Borate.

Compounds	Colour	Decomposition Temp.(°C)	Yield (%)	Analysis (%) Found(Calcd.)				
				C	H	N	M	Cl
$K^+(C_{24}H_{19}N_3B)^-$	Colourless	296	68	71.03 (72.18)	4.67 (4.76)	10.46 (10.52)	-	-
$Cr(C_{24}H_{19}N_3B)_2Cl$	Brown	275	67	69.12 (71.33)	4.58 (4.71)	10.29 (10.40)	6.38 (6.44)	4.37 (4.39)
$Mn(C_{24}H_{19}N_3B)Cl$	Brown	280	66	62.92 (63.93)	4.11 (4.22)	9.26 (9.32)	12.20 (12.21)	7.71 (7.88)
$Fe(C_{24}H_{19}N_3B)_2Cl$	Yellow	278	64	68.95 (70.98)	4.69 (4.68)	10.27 (10.35)	6.95 (6.90)	4.29 (4.37)
$Co(C_{24}H_{19}N_3B)Cl$	Pink	283	76	63.78 (63.37)	4.09 (4.18)	9.15 (9.24)	12.89 (12.98)	7.82 (7.81)
$Ni(C_{24}H_{19}N_3B)Cl$	Green	270	68	63.53 (63.40)	4.17 (4.18)	9.18 (9.25)	12.85 (12.93)	7.78 (7.82)
$Cu(C_{24}H_{19}N_3B)Cl$	Green	285	74	61.05 (62.75)	4.08 (4.14)	9.19 (9.15)	13.71 (13.84)	7.62 (7.74)
$Zn(C_{24}H_{19}N_3B)Cl$	White	275	68	61.89 (62.48)	4.15 (4.13)	9.06 (9.12)	14.07 (14.18)	7.68 (7.71)

Table III. Colour, Decomposition Temperature, % Yield and Analytical Data of the Complexes of Tetrakis(Indolyl)Borate.

Compounds	Colour	Decom-position Temp.(°C)	Yield (%)	Analysis(%) Found(Calcd.)				
				C	H	N	M	Cl
$K^+(C_{32}H_{24}N_4B)^-$	Colour-less	280	64	73.58 (74.70)	4.56 (4.67)	10.73 (10.89)	-	-
$Cr(C_{32}H_{24}N_4B)_2Cl$	Brown	275	68	72.87 (74.03)	4.51 (4.63)	10.62 (10.79)	4.89 (5.02)	3.34 (3.42)
$Mn(C_{32}H_{24}N_4B)Cl$	Brown	281	65	66.78 (67.91)	4.19 (4.25)	9.82 (9.91)	9.68 (9.73)	6.29 (6.28)
$Fe(C_{32}H_{24}N_4B)_2Cl$	Yellow	270	69	72.28 (73.73)	4.69 (4.61)	10.83 (10.75)	5.32 (5.38)	3.39 (3.41)
$Co(C_{32}H_{24}N_4B)Cl$	Pink	285	68	66.02 (67.43)	4.16 (4.21)	9.76 (9.83)	10.39 (10.36)	6.17 (6.24)
$Ni(C_{32}H_{24}N_4B)Cl$	Green	280	72	67.68 (67.46)	4.18 (4.21)	9.72 (9.83)	10.24 (10.32)	6.19 (6.24)
$Cu(C_{32}H_{24}N_4B)Cl$	Green	268	67	64.98 (66.89)	4.19 (4.18)	9.67 (9.76)	11.03 (11.07)	6.08 (6.18)
$Zn(C_{32}H_{24}N_4B)Cl$	White	266	68	66.76 (66.68)	4.13 (4.18)	9.78 (9.73)	11.24 (11.25)	6.18 (6.17)

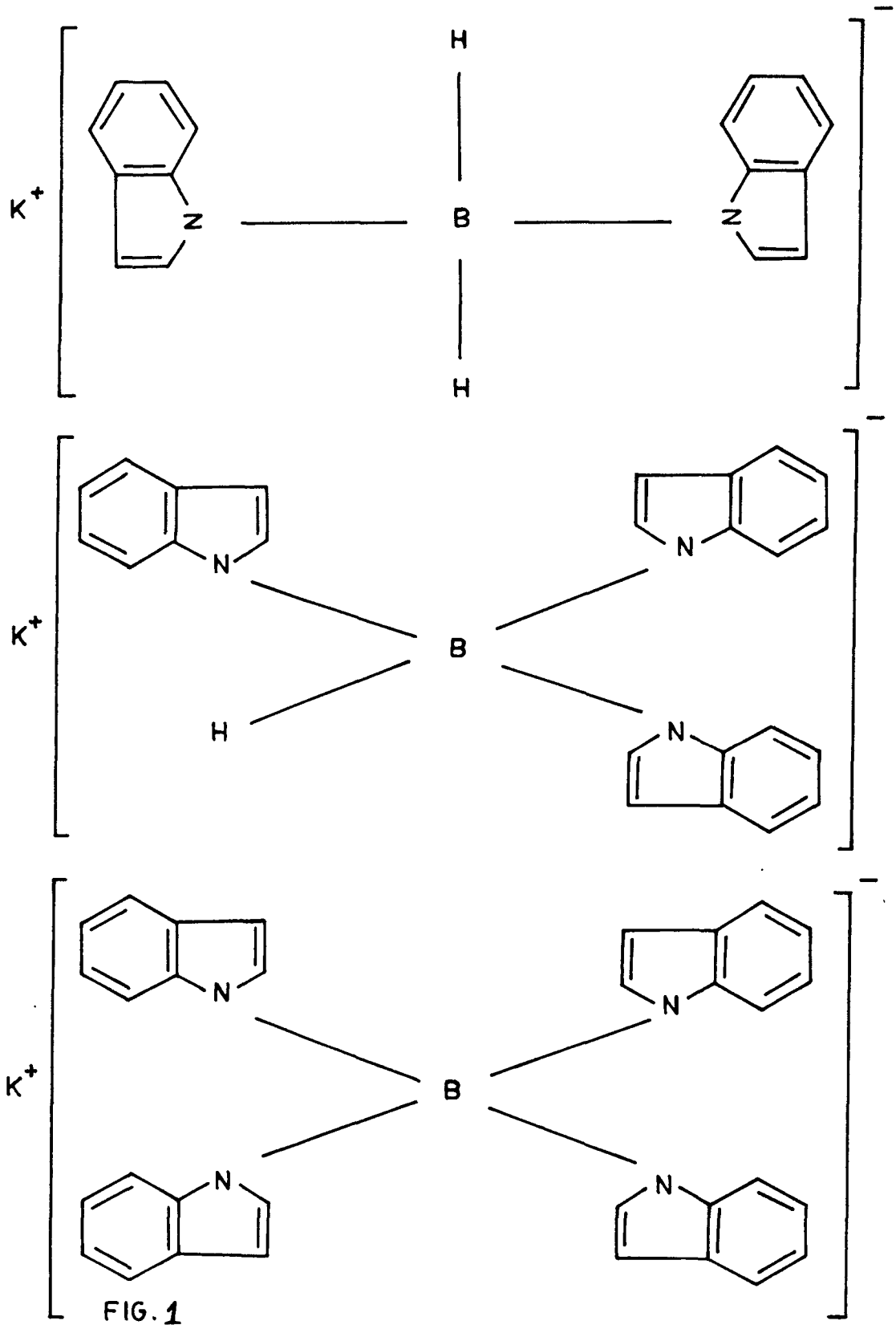


FIG. 1

Table IV. I.R. Spectra of Potassium Dihydrobis(Indolyl)Borate and its Complexes.

Compounds	B-H Stretching (Cm^{-1})	B-N Stretching (Cm^{-1})	C-N Stretching (Cm^{-1})	M-N Stretching (Cm^{-1})
$K^{+}(C_{16}H_{14}N_2B)^{-}$	2420 m 2380 m	1390 m	1352 m	-
$Cr(C_{16}H_{14}N_2B)_2Cl$	2425 m 2380 m	1400 m	1350 m	420 w
$Mn(C_{16}H_{14}N_2B)Cl$	2425 m 2360 m	1390 s	1348 s	410 w
$Fe(C_{16}H_{14}N_2B)_2Cl$	2420 m 2365 m	1390 m	1349 m	405 w
$Co(C_{16}H_{14}N_2B)Cl$	2415 m 2360 m	1385 m	1342 s	400 w
$Ni(C_{16}H_{14}N_2B)Cl$	2420 m 2375 m	1375 m	1345 s	410 w
$Cu(C_{16}H_{14}N_2B)Cl$	2420 s 2360 m	1390 s	1347 m	390 w
$Zn(C_{16}H_{14}N_2B)Cl$	2425 w 2370 w	1385 m	1342 m	400 w

s = strong, m = medium, w = weak

Table V. I.R. Spectra of Potassium Hydrotris(Indolyl)Borate and its Complexes.

Compounds	B-H Stretching (Cm^{-1})	B-N Stretching (Cm^{-1})	C-N Stretching (Cm^{-1})	M-N Stretching (Cm^{-1})
$K^{+}(C_{24}H_{19}N_3B)^{-}$	2410 m	1390 m	1348 m	-
$Cr(C_{24}H_{19}N_3B)_2Cl$	2420 m	1375 m	1345 m	415 w
$Mn(C_{24}H_{19}N_3B)Cl$	2400 m	1385 m	1346 s	420 w
$Fe(C_{24}H_{19}N_3B)_2Cl$	2400 m	1395 m	1344 s	425 w
$Co(C_{24}H_{19}N_3B)Cl$	2425 m	1390 m	1342 m	410 w
$Ni(C_{24}H_{19}N_3B)Cl$	2400 m	1385 m	1343 m	430 w
$Cu(C_{24}H_{19}N_3B)Cl$	2400 m	1380 m	1344 m	385 w
$Zn(C_{24}H_{19}N_3B)Cl$	2400 m	1390 m	1342 m	400 w

s = strong, m = medium, w = weak

Table VI. I.R. Spectra of Potassium Tetrakis(Indolyl)Borate and its Complexes.

Compounds	B–N Stretching (Cm^{-1})	C–N Stretching (Cm^{-1})	M–N Stretching (Cm^{-1})
$K^{+}(C_{32}H_{24}N_4B)^{-}$	1395 m	1345 m	–
$Cr(C_{32}H_{24}N_4B)_2Cl$	1390 m	1338 m	410 w
$Mn(C_{32}H_{24}N_4B)Cl$	1385 m	1342 s	425 w
$Fe(C_{32}H_{24}N_4B)_2Cl$	1395 m	1340 s	420 w
$Co(C_{32}H_{24}N_4B)Cl$	1390 m	1344 m	410 w
$Ni(C_{32}H_{24}N_4B)Cl$	1380 m	1342 m	425 w
$Cu(C_{32}H_{24}N_4B)Cl$	1385 m	1343 m	380 w
$Zn(C_{32}H_{24}N_4B)Cl$	1390 m	1340 m	400 w

s = strong, m = medium, w = weak

Complexes of Dihydrobis(Indolyl) Borate Anion

In case of Cr(III) and Fe(III) complexes the magnetic moment values are well within the range consistent with an octahedral (54) geometry (Table VII). The electronic spectrum of the Cr(III) exhibit weak bands at 23,254 cm^{-1} and 16,667 cm^{-1} which may reasonably be assigned to $^4T_{1g}(F) \longleftarrow {}^4A_{2g}(F)$ and $^4T_{2g}(F) \longleftarrow {}^4A_{2g}(F)$ transitions, respectively. Likewise, Fe(III) also shows two bands observed at 23,255 cm^{-1} and 20,202 cm^{-1} assigned to $^4T_{2g}(G) \longleftarrow {}^6A_{1g}$ and $^4T_{1g}(G) \longleftarrow {}^6A_{1g}$ transitions, respectively, magnetic moment of Fe(III) ion (5.81BM) is consistent with five unpaired electrons. They both presumably achieve an octahedral geometry by bridging chlorine atom.

The magnetic moments (5.78, 4.71 and 3.65 BM) observed for Mn(II), Co(II) and Ni(II) complexes indicate a tetrahedral geometry as has been found in similar other cases (55). In the case of Mn(II) complex the electronic spectrum exhibits three bands at 23,809 cm^{-1} 22,222 cm^{-1} and 20,202 cm^{-1} corresponding to $^4A_1(G) \longleftarrow {}^6A_1$, $^4T_2(G) \longleftarrow {}^6A_1$ and $^4T_1(G) \longleftarrow {}^6A_1$ transitions, respectively. Co(II) shows only one hand at 15,151 cm^{-1} assigned to $^4T_1(P) \longleftarrow {}^4A_2(F)$ transition. Ni(II) complex has also been found to display only one band observed at 16,394 cm^{-1} assigned to $^3T_1(P) \longleftarrow {}^3T_1(F)$ transition.

It is difficult to distinguish between a square planar and a tetrahedral geometry for Cu(II) ion only on the basis of d-d transitions as it occurs in the same region for both the

Table VII. Magnetic Susceptibility, Electronic Spectra and Ligand Field Parameters for the Potassium Dihydrobis(Indolyl)Borate Complexes.

Compounds	μeff (B.M.)	Electronic Bands (Cm^{-1})	Possible Assignments	10Dq (Cm^{-1})	B (Cm^{-1})	β
$Cr(C_{16}H_{14}N_2B)_2Cl$	3.81	40,816	C.T.	16,667	724	0.71
		23,254	$^4T_{1g}(F) \longleftarrow {}^4A_{2g}(F)$			
		16,667	$^4T_{2g}(F) \longleftarrow {}^4A_{2g}(F)$			
$Mn(C_{16}H_{14}N_2B)Cl$	5.78	42,553	C.T.	-	-	.
		23,809	$^4A_1(G) \longleftarrow {}^6A_1$			
		22,222	$^4T_2(G) \longleftarrow {}^6A_1$			
		20,202	$^4T_1(G) \longleftarrow {}^6A_1$			
$Fe(C_{16}H_{14}N_2B)_2Cl$	5.81	41,666	C.T.	13,843	921	0.86
		23,255	$^4T_{2g}(G) \longleftarrow {}^6A_{1g}$			
		20,202	$^4T_{1g}(G) \longleftarrow {}^6A_{1g}$			
$Co(C_{16}H_{14}N_2B)Cl$	4.71	40,816	C.T.	-	-	-
		18,518	C.T.			
		15,151	$^4T_1(P) \longleftarrow {}^4A_2(F)$			
$Ni(C_{16}H_{14}N_2B)Cl$	3.65	43,478	C.T.			
		16,394	$^3T_1(P) \longleftarrow {}^3T_1(F)$	-	-	-
$Cu(C_{16}H_{14}N_2B)Cl$	1.78	40,000	C.T.			
		29,411	C.T.			
$Zn(C_{16}H_{14}N_2B)Cl$	Diamag.	-	-	-	-	-

C.T. = Charge transfer

geometries. However, the magnetic moment value extending over a range of 1.78 - 1.99BM for Cu(II) complexes is indicative of a square planar geometry as has been found in the crystal structure of dimeric hydroxamate complex of Cu(II) ion (56) with a magnetic moment value of 1.78BM. In the absence of any band and the magnetic moment value (1.78BM), Cu(II) in dihydro-bis(indolyl) borate is tentatively suggested to be square planar with chlorine bridging (Fig.2). This is in keeping with the tetrahedral geometry of boron in the complex.

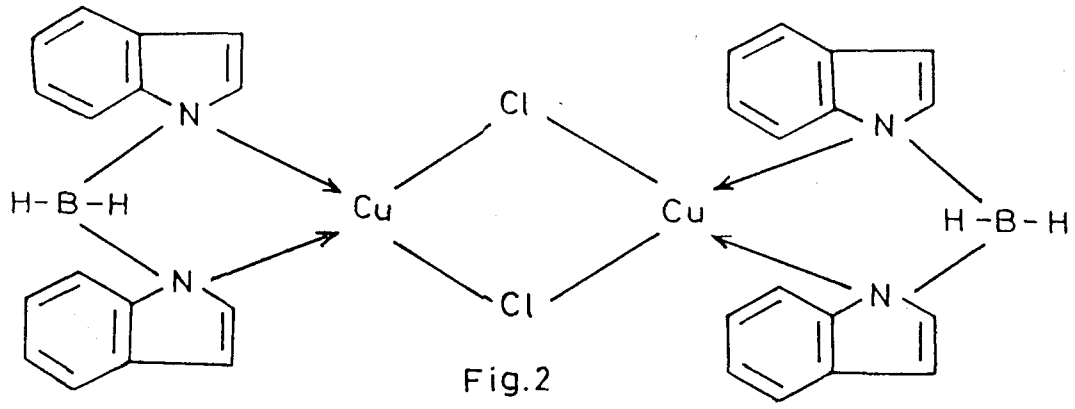


Fig.2

Complexes of Hydrotris (Indolyl) Borate Anion

In case of Cr(III) and Fe(III) complexes the observed magnetic moments (3.67 and 5.83BM) are quite close to the calculated value for an octahedral geometry with A ground term (54). The reflectance spectrum (Table VIII) of the Cr(III) complex exhibits three bands at 36,363 cm^{-1}, 24,392 cm^{-1} and 17,240 cm^{-1} assignable to $^4T_{1g}(P) \longleftarrow {}^4A_{2g}(F)$, $^4T_{1g}(F) \longleftarrow {}^4A_{2g}(F)$ and $^4T_{2g}(F) \longleftarrow {}^4A_{2g}(F)$ transitions, respectively. The appearance of only two bands at 23,809 cm^{-1} and 19,230 cm^{-1} in Fe(III) are due to $^4T_{2g}(G) \longleftarrow {}^6A_{1g}$ and $^4T_{1g}(G) \longleftarrow {}^6A_{1g}$ transitions, respectively.

The magnetic moment value of 5.59BM for Mn(II) complex is slightly less than that required for five unpaired electrons for tetrahedral geometry. It may be attributed to the magnetically non-dilute nature of the complex (57). Normally there appears one charge transfer band at 40,816 cm^{-1} but three weak bands observed at 24,096 cm^{-1}, 22,321 cm^{-1} and 21,276 cm^{-1} are assigned to $^4A_1(G) \longleftarrow {}^6A_1$, $^4T_2(G) \longleftarrow {}^6A_1$ and $^4T_1(G) \longleftarrow {}^6A_1$ transitions, respectively.

The magnetic moments (4.74 and 3.62BM) observed for the Co(II) and Ni(II) complexes are close to those expected for tetrahedral geometry (55). The Co(II) complex exhibited a high frequency band at 15,387 cm^{-1} attributed to $^4T_1(P) \longleftarrow {}^4A_2(F)$ transition. The other bands could not be observed as they were beyond the range of the instrument. The Ni(II) complex has only

Table VIII. Magnetic Susceptibility, Electronic Spectra and Ligand Field Parameters for the Potassium Hydrotris(Indolyl)Borate Complexes.

Compounds	μeff (B.M.)	Electronic bands(Cm^{-1})	Possible Assignments	10Dq (Cm^{-1})	B (Cm^{-1})	β
$Cr(C_{24}H_{19}N_3B)_2Cl$	3.67	40,000	C.T.	17,240	783	0.75
		36,363	$^4T_{1g}(P) \longleftarrow {}^4A_{2g}(F)$			
		24,392	$^4T_{1g}(F) \longleftarrow {}^4A_{2g}(F)$			
		17,240	$^4T_{2g}(F) \longleftarrow {}^4A_{2g}(F)$			
$Mn(C_{24}H_{19}N_3B)Cl$	5.59	40,816	C.T.	-	-	-
		24,096	$^4A_1(G) \longleftarrow {}^6A_1$			
		22,321	$^4T_2(G) \longleftarrow {}^6A_1$			
		21,276	$^4T_1(G) \longleftarrow {}^6A_1$			
$Fe(C_{24}H_{19}N_3B)_2Cl$	5.83	40,000	C.T.	12,809	914	-
		23,809	$^4T_{2g} \longleftarrow {}^6A_{1g}$			
		19,230	$^4T_{1g} \longleftarrow {}^6A_{1g}$			
$Co(C_{24}H_{19}N_3B)Cl$	4.74	43,478	C.T.	-	-	-
		28,057	C.T.			
		15,387	$^4T_1(P) \longleftarrow {}^4A_2(F)$			
$Ni(C_{24}H_{19}N_3B)Cl$	3.62	42,553	C.T.	-	-	-
		28,985	C.T.			
		16,129	$^3T_1(P) \longleftarrow {}^3T_1(F)$			
$Cu(C_{24}H_{19}N_3B)Cl$	1.80	29,850	C.T.	-	-	-
		27,777	C.T.			
$Zn(C_{24}H_{19}N_3B)Cl$	Diamag.	-	-	-	-	-

C.T. = Charge transfer

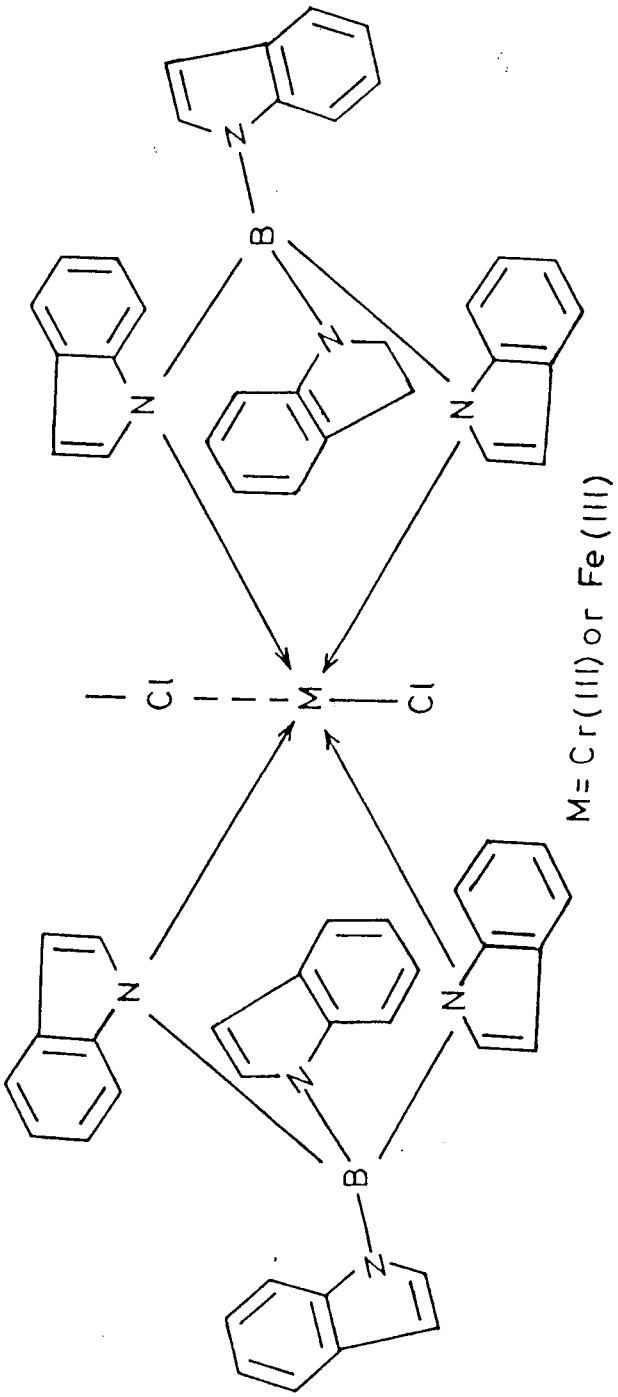
one band at 16,129 cm^{-1} arising out of the transition $^3T_1(P) \longleftarrow {}^3T_1(F)$. The other expected bands in the region 8000-7000 cm^{-1} were out of the range of the instrument.

The Cu(II) complex with hydrotris(indolyl) borate ligand may either be monomeric tetrahedral or dimeric binuclear square planar. It is proposed to be dimeric square planar because it is relatively more stable than the corresponding monomeric species(56).

Complexes of Tetrakis (Indolyl) Borate Anion

The observed magnetic moment for the Cr(III) complex close to that calculated for an octahedrallysurrounded metal ion(Fig.3). The band observed at 45,454 cm^{-1} in the electronic spectrum (Table IX) has been assigned to charge transfer. The electronic spectrum also shows bands at 36,363 cm^{-1} and 24,096 cm^{-1} assignable to $^4T_{1g}(P) \longleftarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \longleftarrow {}^4A_{2g}(F)$ transitions, respectively, characteristic of an octahedral geometry (58).

The observed magnetic moment value for the Mn(II) complex is 5.80 B.M. and is also very close to that calculated for the metal in an octahedral environment. The electronic spectrum shows an intense charge transfer band at 41,666 cm^{-1}. The octahedral geometry of this complex has been further substantiated by the appearance of bands at 25,000 cm^{-1}, 23,753 cm^{-1} and 19,048 cm^{-1} assigned to the $^4A_{1g}(G) \longleftarrow {}^6A_{1g}$, $^4T_{2g}(G) \longleftarrow {}^6A_{1g}$ and $^4T_{1g}(G) \longleftarrow {}^6A_{1g}$ transitions, respectively, in its electronic spectrum.



M = Cr(III) or Fe(III)

Fig. 3

Table IX. Magnetic Susceptibility, Electronic Spectra and Ligand Field Parameters for the Potassium Tetrakis(Indolyl)Borate Complexes.

Compounds	μeff (B.M.)	Electronic bands (Cm^{-1})	Possible Assignments	10Dq (Cm^{-1})	B (Cm^{-1})	β
$Cr(C_{32}H_{24}N_4B)_2Cl$	3.73	45,454	C.T.	17,140	901	0.88
		36,363	$^4T_{1g}(P) \longleftarrow {}^4A_{2g}(F)$			
		24,096	$^4T_{1g}(F) \longleftarrow {}^4A_{2g}(F)$			
$Mn(C_{32}H_{24}N_4B)Cl$	5.80	41,666	C.T.	10,778	828	0.86
		25,000	$^4A_{1g}(G) \longleftarrow {}^6A_{1g}$			
		23,753	$^4T_{2g}(G) \longleftarrow {}^6A_{1g}$			
		19,048	$^4T_{1g}(G) \longleftarrow {}^6A_{1g}$			
$Fe(C_{32}H_{24}N_4B)_2Cl$	5.84	40,816	C.T.	–	–	–
		17,094	$^4T_{1g}(G) \longleftarrow {}^6A_{1g}$			
		22,471	$^4T_{2g}(G) \longleftarrow {}^6A_{1g}$			
$Co(C_{32}H_{24}N_4B)Cl$	4.78	43,478	C.T.	10,891	989	0.87
		23,809	$^4T_{1g}(P) \longleftarrow {}^4T_{1g}(F)$			
		10,870	$^4T_{2g}(F) \longleftarrow {}^4T_{1g}(F)$			
$Ni(C_{32}H_{24}N_4B)Cl$	3.71	40,816	C.T.	10,211	890	0.83
		25,316	$^3T_{1g}(P) \longleftarrow {}^3A_{2g}(F)$			
		14,388	$^3T_{1g}(F) \longleftarrow {}^3A_{2g}(F)$			
$Cu(C_{32}H_{24}N_4B)Cl$	1.76	41,666	C.T.	12,345	–	–
		27,777	C.T.			
		12,345	$^2T_{2g} \longleftarrow {}^2E_g$			
$Zn(C_{32}H_{24}N_4B)Cl$	Diamag.	–	–	–	–	–

C.T. = Charge transfer

The magnetic moment of 5.84 B.M of Fe(III) complex clearly indicates an octahedral geometry about this metal ion(Fig. 3). Its electronic spectrum exhibits well resolved bands at 17,094 cm^{-1} and 22,471 cm^{-1} characteristic of an octahedral array of ligands around the metal ion. The more intense band at 40,816 cm^{-1} may be assigned to charge transfer.

The magnetic moment value of 4.78 B.M. for the Co(II) complex indicates an octahedral geometry around the metal ion. The electronic band observed at 43,478 cm^{-1} is attributed to charge transfer. The bands observed at 23,809 cm^{-1} and 10,870 cm^{-1} assigned to $^4T_{1g}(P) \longleftarrow {}^4T_{1g}(F)$ and $^4T_{2g}(F) \longleftarrow {}^4T_{1g}(F)$ transitions, respectively are also suggestive of an octahedral geometry for this complex.

The Ni(II) complex shows a magnetic moment value of 3.71 B.M. characteristic of an octahedral complex. The electronic spectrum shows intense charge transfer band at 40,816 cm^{-1}. The two bands observed in the electronic spectrum at 25,316 cm^{-1} and 14,388 cm^{-1} are reasonably assigned to $^3T_{1g}(P) \longleftarrow {}^3A_{2g}(F)$ and $^3T_{1g}(F) \longleftarrow {}^3A_{2g}(F)$ transitions, respectively characteristic of an octahedral environment around the nickel ion.

The magnetic moment of 1.76 B.M. of Cu(II) complex clearly indicates an octahedral geometry about this metal ion. The electronic spectrum exhibits charge transfer bands at 41,666 cm^{-1} and 27,777 cm^{-1}. However, the weak band observed at 12,345 cm^{-1} assigned to $^2T_{2g} \longleftarrow {}^2E_g$ transition is characteristic of an octahedral geometry for the d^9 system.

The tetrakis ligand seems to be analogous to the hydrotris ligand in its coordinating behaviour. It has been observed that the magnetic moment data for the complexes of hydrotris ligand were in some cases lower than the expected value and this has been attributed to the non-dilute nature of these complexes (59, 60). It has also been observed that the tetrakis ligand differs from the dihydrobis and hydrotris ligand in that the former gives rise to octahedral complexes whereas the latter two yield octahedral as well as in some cases tetrahedral and square planar geometries.

The nephelauxetic parameter, 'β', evaluated for the complexes compares well with values for similar complexes. The 'β' value in these cases falls below unity demonstrating low degree of covalency and the ligand may be placed in the vicinity of ethylene diamine in the nephelauxetic series (61).

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